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Effect of Varying the Volatilization of Methyl Bromide by Combinations With Various Solvents on Its Distribution in BULK GRAIN FUMIGATION

N. M. Dennis and W. K. Whitney, Stored-Grain Insects Laboratory, Manhattan, Kans.[1]

SUMMARY

Laboratory studies in cooperation with the Michigan Chemical Corporation were made to investigate under controlled conditions the behavior of methyl bromide and mixtures of methyl bromide with various solvents, in the fumigation of bulk wheat and milled products. The studies included space fumigation in the absence of any commodity, fumigation of bulk wheat and of milled products using natural diffusion for distribution, and forced recirculation of the fumigants through wheat.

Cylindrical test chambers 6 feet high by 7-7/8 inches inside diameter were used. In some instances these were fitted with a blower and return duct to establish recirculation of the fumigant vapor. The methyl bromide component was analyzed to determine concentrations present at selected locations and exposures. Test insects, the rice weevil and the confused flour beetle, and gas sampling points were located at 18-inch intervals from top to bottom of the chambers to determine the extent of penetration into commodities.

The tests demonstrated that:

Changing the rate of volatilization of methyl bromide by mixing it with higher boiling-point solvents did not materially change the amount of methyl bromide component associated with complete mortality of test insects in space fumigation. The penetration of methyl bromide into wheat, when applied to the surface, was materially enhanced by mixing it with higher boiling-point solvents. The mixture having the methyl bromide component with the slowest rate of volatilization was the most efficient in promoting diffusion of methyl bromide to the bottom of the test chambers, when applied to the surface of the wheat. Venting the bottom of test chambers filled with wheat, or installing a return duct to the top of a sealed chamber caused a downward convection that accelerated penetration. There was no particular difference in open-top and sealed chambers filled with wheat in rate of penetration when the bottom was not vented. Dosages applied to milled products equal to or greater than those used on wheat resulted in much less penetration. Recirculation of methyl bromide through the wheat resulted in uniform distribution and greatly increased efficiency. The recirculation of a mixture of ethyl acetate and methyl bromide (9-1) through wheat did not lessen the amount of the methyl bromide component sorbed by the wheat, as reflected by the concentration present after 20 hours, in comparison to the amount of methyl bromide sorbed when applied alone.

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[1] This laboratory is one of the field stations of the Stored-Product Insects Section, Biological Sciences Branch, Marketing Research Division, Agricultural Marketing Service, United States Department of Agriculture.

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BACKGROUND AND PURPOSE OF STUDY

Methyl bromide is an exceedingly useful fumigant for the treatment of packaged food and feed products, because of its high toxicity to insects, its facility in penetrating packaged commodities, and its relatively low sorption ratio. The behavior of methyl bromide gas in the fumigation of bulk products, such as grain, is not well understood. When applied to bulk grain in bins, freight cars, or other deep containers, the gas, though heavier than air, does not readily penetrate the grain mass unless it is drawn through by mechanically induced air currents. On the other hand, if mixed with higher boiling-point solvents, satisfactory gas distribution and good insect control can be obtained with the conventional method of applying the fumigant mixture as a liquid to the grain surface. It has also been successfully used as a local or spot fumigant in milling machinery when combined with certain high boiling-point solvents.

A laboratory study was undertaken in cooperation with the Michigan Chemical Corporation, St. Louis, Mich., to investigate, under controlled conditions, the behavior of methyl bromide, and mixtures of methyl bromide in various solvents, in the fumigation of bulk grain and milled products.

The studies included observations made under three sets of conditions: (1) space fumigation in the absence of any commodity, (2) natural diffusion in bulk commodities, and (3) forced recirculation of fumigants through wheat.

TECHNIQUES AND MATERIALS

Test chambers

The test chambers were cylindrical, 6 feet high and 7-7/8 inches in inside diameter. Several chambers were made from open-end 12-inch glass cylinders with ground edges. The edges were fastened together with 1-inch plastic electrician's tape. The ends of the 6-foot cylinder were closed by taping on discs of tempered masonite which had been impregnated with hot paraffin to prevent sorption of the fumigants (fig. 1). Other test chambers were made of galvanized sheet metal. Three metal chambers (fig. 2) and one glass chamber were equipped with blowers and return ducts so that the fumigant could be recirculated. The test chambers were placed vertically side by side so that paired experiments could be run simultaneously under the same conditions of atmospheric pressure, humidity, and temperature. No differences were observed in the results between the glass and metal chambers.

All joints, connections, and closures were checked before each test to be sure that they were tight, and during the exposure period additional checks were made with a halide detector. Trial tests demonstrated that these chambers were reasonably leakproof, and sorption on the chamber walls was so low as to be practically nondetectable.

In recirculation tests the rate of air or gas flow through the commodity was determined by a gas meter connected to the return duct. The recirculation systems were used to aerate the commodities after each test was completed.

Formulations

Three acetates and carbon tetrachloride were the solvents used in these tests. The acetates were selected because they did not interfere with the analysis for methyl bromide by the modified Volhard method, and carbon tetrachloride because it is commonly used as a component of many grain fumigants. Ethyl acetate, n-propyl acetate, and n-butyl acetate were selected to give the desired differences in the rate of volatilization of methyl bromide mixed with them. They were also known to have reasonably similar toxicities to the granary weevil (Sitophilus granarius (L.)). The physical properties and relative toxicities to the granary weevil are given in table 1.

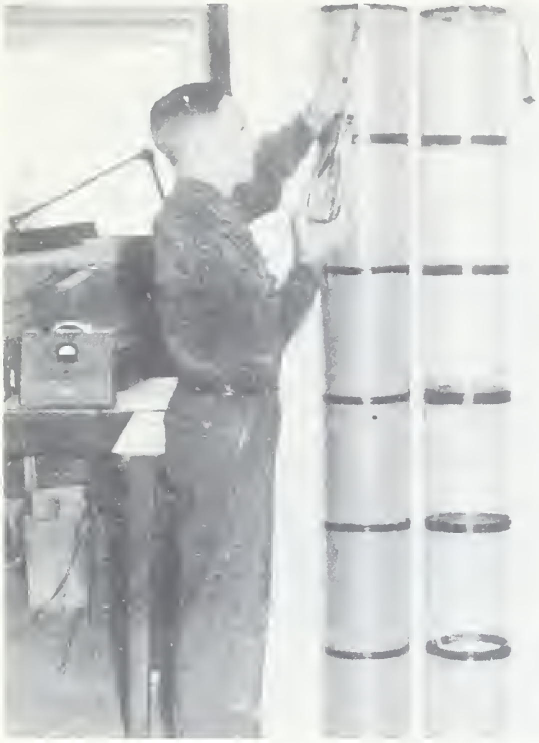

FIGURE 1. --Test chambers made of sections of glass cylinders. The one on the left is filled with wheat, the other is empty. An insect test cage is shown projecting through the cover of the chamber on the right. The operator is withdrawing a sample of gas.

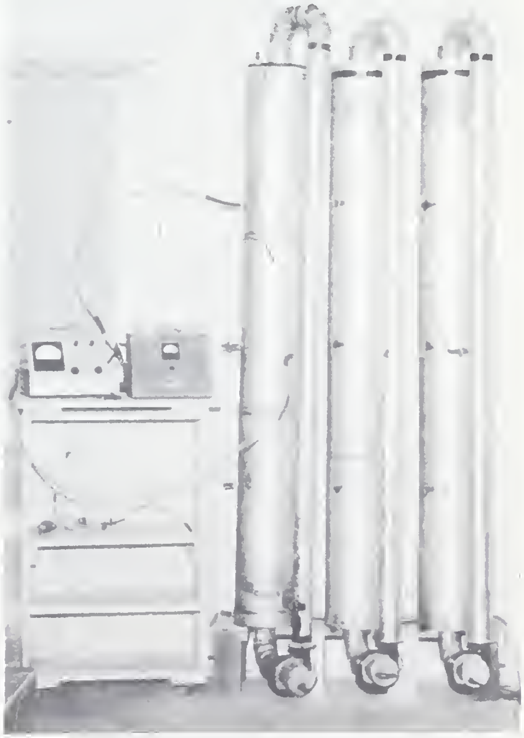

FIGURE 2. --Metal test chambers. These are equipped with blowers and return ducts for recirculating fumigants through wheat. A thermal conductivity gas analyzer is attached to the one on the left. The gas sample is withdrawn through the top tube, passed through the instrument, and returned to the cylinder through the lower tube.

TABLE 1.--Physical properties[1] and comparative toxicities of methyl bromide and selected solvents to the granary weevil[2]

Material	Molecular weight	Boiling point (° C.)	Specific gravity	Minimum lethal dosage (Mg/l, 24-hr. exposure)
Methyl bromide...............	94.95	4.5	1.732 @ 0° C.	3.3
Ethyl acetate................	88.1	77.1	0.901 @ 20° C.	56.0
n-propyl acetate.............	102.1	101.6	0.886 @ 20° C.	33.0
n-butyl acetate..............	116.2	125.0	0.882 @ 20° C.	11.2
Carbon tetrachloride.........	153.8	76.7	1.589 @ 25° C.	275.0

[1] Lange, N. A. 1946. Handbook of Chemistry. Ed. 6.
[2] Ferguson, J. and H. Pirie. 1948. The toxicity of vapors to the grain weevil. Ann. Appl. Biol. 35:532-550.

The following formulations were used in the studies on a weight/weight basis:

1. Ethyl acetate - methyl bromide (9-1)
2. n-propyl acetate - methyl bromide (9-1)
3. n-butyl acetate - methyl bromide (9-1)
4. Carbon tetrachloride - methyl bromide (9-1)
5. Carbon tetrachloride - methyl bromide (4-1)
6. Carbon tetrachloride - methyl bromide (1-1)
7. Carbon tetrachloride - methyl bromide (1-4)

Data developed in the chemical laboratory of the Michigan Chemical Corporation by L. E. Pauling[2] demonstrated that there was an increase in the percent of methyl bromide in the total product of volatilization of the 9-1 mixtures with the acetates, as the boiling point of the solvent increased, but that there was no pronounced decrease in the vapor pressure of the mixtures (tables 2 and 3). These findings are in agreement with Raoult's Law concerning partial pressures of mixtures.

TABLE 2.--Rate of methyl bromide volatilization from 225 grams of 9-1 mixtures with selected acetate solvents, with 8 liters of air moving over the mixtures each hour

Hours at 20° C.	Ethyl acetate - methyl bromide mixture	n-propyl acetate - methyl bromide mixture	n-butyl acetate - methyl bromide mixture
	Grams	*Grams*	*Grams*
0........................	0	0	0
1........................	5.5	7.3	7.7
2........................	9.0	11.0	12.0
3........................	12.0	14.5	15.2
4........................	14.5	17.0	18.2
5........................	16.7	19.0	20.0
6........................	18.7	20.5	21.5
7........................	20.5	21.5	22.5
8........................	21.5	22.5	--
9........................	22.5	--	--

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[2] Pauling, L. E. Vapor pressures and comparative volatilities of mixtures of methyl bromide and various acetate solvents. Unpublished report, Div. Stored-Product Insect Invest., U. S. Dept. Agr., Nov. 24, 1953.

TABLE 3.--Vapor pressure and percentage of methyl bromide in the total product of vaporization of mixtures of acetates and methyl bromide (9-1)

Mixture	Vapor pressure (mm. at 20° C.)	Percent by weight of methyl bromide in vapor
Ethyl acetate - methyl bromide......	147	59
n-propyl acetate - methyl bromide...	127	85
n-butyl acetate - methyl bromide....	107	93.5
Methyl bromide......................	1,580 (at 25° C.)	100.0

The mixtures of acetates and methyl bromide were prepared at St. Louis, Mich., and shipped to Manhattan where they were kept under refrigeration. The small amount needed for each test was withdrawn from the supply into a test tube immersed in a solution of salt water and ice. The actual dosage was measured with a pipette or graduated cylinder, at about 0° F. The mixtures of carbon tetrachloride and methyl bromide were prepared at Manhattan, and were handled in the same manner.

Analysis of gas samples

The concentration of methyl bromide at various locations and at various time intervals was determined by analysis of gas samples withdrawn from the selected locations through 1/4-inch O. D. plastic or copper tubing. In tests where methyl bromide was dissolved in one of the acetate solvents, or in some instances where methyl bromide alone was involved, a modified Volhard method of gas analysis was used. In this technique the sample was drawn into an evacuated quart milk bottle which contained monoethanolamine as an absorbent. After the methyl bromide was absorbed, the sample was titrated in the same bottle (fig. 3).

A thermal conductivity gas analyzer was used to determine concentrations of methyl bromide and a 9-1 ethyl acetate-methyl bromide mixture. The gas sample was drawn through this instrument from the test chamber and returned to the chamber (fig. 2).

Insect samples

Two species of test insects were used that react differently to various fumigants, the adult rice weevil (Sitophilus oryza (L.)) and the confused flour beetle (Tribolium confusum J. duV.). The rice weevil is more susceptible to methyl bromide than the flour beetle, but less susceptible to fumigants such as hydrocyanic acid. The insects had been reared under conditions of constant temperature and humidity according to long established procedures. Thirty insects of each species were used in each test; they were placed in separate cages that were about half full of clean wheat of 12-percent moisture content. At the end of the exposure period the insects and wheat were removed from the cages, a mortality count was made, and the insects were then placed in small plastic boxes. The boxes were held in the laboratory rearing room until the second and final mortality count was taken on the fifth day.

The insect test cages were constructed of 45-mesh woven bronze wire. Each cylindrical cage was 2 inches long and 11/16 inch in inside diameter. One end was fitted with a paraffin-treated cork (fig. 4).

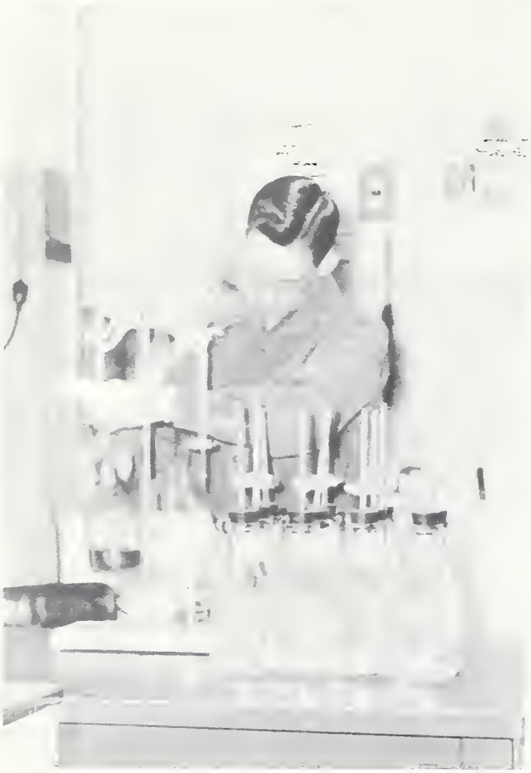
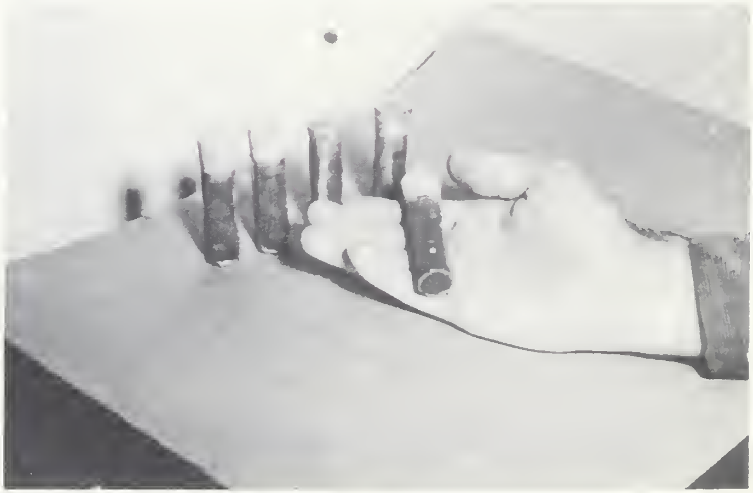


FIGURE 3. --Titration of gas samples by the modified Volhard method.

FIGURE 4. --Insect test cages.



SPACE FUMIGATION TESTS

Procedure

Insect samples were exposed in empty test chambers to determine the amount of methyl bromide associated with complete mortality by each fumigant mixture.

An insect cage was placed at the top, center, and bottom of each empty chamber. The top cage was held directly below the cover by inserting the free end of its cork stopper into a hole in the cover. The other two cages were suspended on a string secured by the stopper of the top cage.

The fumigant mixture was released in liquid form from a pipette inserted through a small hole in the cover, into a shallow glass dish suspended approximately 2 inches below the top, and allowed to evaporate. The insects were exposed to the vapors for 20 hours. The amount of methyl bromide associated with 100-percent mortality was determined on the basis of the applied dosage, not by the analysis of the vapors.

Results

The results are presented in table 4. It was demonstrated that approximately the same amount of methyl bromide was associated with 100-percent mortality of the test insects whether the methyl bromide was used alone or in mixtures with solvents. Some effect from the solvent itself should be expected.

TABLE 4.--Amount of methyl bromide alone and in various solvents associated with 100-percent mortality of test insects in empty fumigation chambers

Fumigation mixture	Amount of methyl bromide component introduced (oz. per 1,000 cu. ft.)	
	Rice weevil	Flour beetle
1. Ethyl acetate - methyl bromide (9-1).........	2.27	4.83
2. n-propyl acetate - methyl bromide (9-1)......	2.86	4.49
3. n-butyl acetate - methyl bromide (9-1).......	2.24	4.48
4. Carbon tetrachloride - methyl bromide (9-1)..	2.70	4.80
5. Carbon tetrachloride - methyl bromide (4-1)..	2.40	4.50
6. Carbon tetrachloride - methyl bromide (1-1)..	2.10	4.80
7. Carbon tetrachloride - methyl bromide (1-4)..	2.20	4.80
8. Methyl bromide.............................	2.70	5.10

NATURAL DIFFUSION IN BULK COMMODITIES

Procedure

The diffusion of methyl bromide and various mixtures of it in solvents in a 6-foot column of wheat, from a surface application, was studied by determining the mortality of insects placed at the surface, and at the 18-, 36-, 54-, and 72-inch (bottom) levels after 20 hours of exposure, and by taking gas samples at the surface, middle, and bottom levels at the end of the 20 hours. The dosage rates were increased by modest increments until 100-percent mortality occurred in all sample locations or until the dosage exceeded a practical limit (table 8). The amount of methyl bromide related to the dosage rate of each formulation was the basis of comparing the efficiency of penetration of each. The analysis of gas present at the 20-hour period was a corroboration of the above calculation.

Five different arrangements to induce different convection conditions were tested: (1) sealed test chamber; (2) chamber with open top; (3) sealed chamber with vent from bottom to top; (4) chamber with bottom vented; and (5) chamber with top and bottom vented.

The rate of penetration of the test formulations into several milled products of different degrees of fineness--bran, shorts, middlings, and flour--was also studied by the same technique.

Results

Wheat. The results of the tests with wheat are presented in tables 5, 6, and 7.

TABLE 5.--The amount of methyl bromide associated with 100-percent mortality of test insects at 5 locations in sealed and open-top 6-foot test chambers filled with wheat, and the amounts present at the end of 20 hours of exposure

Rice weevil

Fumigant mixture	Amount of methyl bromide associated with complete mortality at bottom		Depth of gas sample in wheat	Amount of methyl bromide recovered after 20 hours	
	Sealed chamber	Open-top chamber		Sealed chamber	Open-top chamber
	Oz. per 1,000 cu. ft.	*Oz. per 1,000 cu. ft.*	*Inches*	*Oz. per 1,000 cu. ft.*	*Oz. per 1,000 cu. ft.*
1. Ethyl acetate - methyl bromide (9-1)	51.84	51.84	0	5.8	0.6
			36	9.2	7.2
			72	2.8	2.4
2. n-propyl acetate - methyl bromide (9-1)	68.16	68.16	0	--	3.6
			36	10.0	8.8
			72	1.2	2.6
3. n-butyl acetate - methyl bromide (9-1)	84.96	126.56	0	9.6	4.8
			36	7.0	19.6
			72	2.0	2.8
4. Carbon tetrachloride - methyl bromide (9-1)	30.40	44.80	--	--	--
5. Methyl bromide.................	121.60	121.60	0	16.0	2.6
			36	20.2	18.6
			72	1.8	2.6
Flour beetle					
1. Ethyl acetate - methyl bromide (9-1)	69.12	77.76	0	8.8	[1] 1.2
			36	16.6	11.2
			72	2.8	6.1
2. n-propyl acetate - methyl bromide (9-1)	118.56	85.28	0	16.0	1.2
			36	27.6	13.4
			72	4.8	4.8
3. n-butyl acetate - methyl bromide (9-1)	135.04	135.04	0	29.2	--
			36	41.8	20.4
			72	5.0	3.8
4. Carbon tetrachloride - methyl bromide (9-1)	44.80	48.64	--	--	--
5. Methyl bromide.................	182.40	167.20	0	29.8	3.4
			36	53.0	23.0
			72	6.8	4.2

[1] Average for 2 tests.

TABLE 6.--The amount of methyl bromide associated with 100-percent mortality of test insects at 5 locations in a sealed chamber filled with wheat. with a vent from bottom to top, and the amounts present at the end of 20 hours of exposure

Fumigant mixture	Amount of methyl bromide per 1,000 cu. ft. associated with complete mortality	Depth of gas sample in wheat	Amount of methyl bromide per 1,000 cu. ft. recovered after 20 hours from-- Replicates 1	Replicates 2	Replicates 3	Average of replicates
Rice weevil						
	Ounces	*Inches*	*Ounces*	*Ounces*	*Ounces*	*Ounces*
Ethyl acetate - methyl bromide (9-1)	51.84	0	37.8	20.0	37.0	31.6
		18	33.8	35.6	37.0	35.5
		36	19.6	18.6	22.8	20.3
		54	10.0	8.8	8.4	9.1
		72	3.4	1.6	1.0	2.0
Methyl bromide[1]....	60.8	0		54.0		
		18		43.0		
		36		26.0		
		54		12.0		
		72		4.0		
Flour beetle						
Ethyl acetate - methyl bromide (9-1)	51.84	0	37.8	20.0	37.0	31.6
		18	33.8	35.6	37.0	35.5
		36	19.6	18.6	22.8	20.3
		54	10.0	8.8	8.4	9.1
		72	3.4	1.6	1.0	2.0
Methyl bromide[1]....	91.20	0		18.0		
		18		51.0		
		36		47.0		
		54		28.0		
		72		8.0		

[1] Analyses by thermal conductivity method.

The efficiency of the 3 acetate mixtures in promoting penetration of methyl bromide to the bottom of the 6-foot column of wheat, as evidenced by the amount of methyl bromide associated with the dosage rate applied to the top surface, was in the reverse order of the rate at which methyl bromide volatilized from the mixtures. In table 5, the amount of methyl bromide associated with complete mortality of test insects at 5 locations from top to bottom increases in logical increments, with the ethyl acetate - methyl bromide formulation showing the greatest efficiency, n-propyl acetate - methyl bromide next, and n-butyl acetate - methyl bromide the least. The carbon tetrachloride - methyl bromide mixture showed a considerably higher efficiency by this standard but unfortunately the comparative rate of volatilization of methyl bromide from this mixture was not determined, so no comparison can be made. Undiluted methyl bromide exhibited very poor efficiency, as previous experience had demonstrated.

There was no particular difference in the efficiency of penetration in an open-top chamber and in a sealed chamber (table 5). Efficiency appeared to improve when a return vent from bottom to top of a sealed chamber was used (table 6) as evidenced by the

TABLE 7.--The amount of methyl bromide associated with 100-percent mortality of test insects at 5 locations in test chambers filled with wheat, with the top and bottom vented, and the amounts present at the end of 20 hours of exposure

Fumigant mixture	Amount of methyl bromide per 1,000 cu. ft. associated with complete mortality at bottom		Depth of gas sample in wheat	Amount of methyl bromide per 1,000 cu. ft. recovered after 20 hours from --[1]							
				Top closed and bottom vented				Top open and bottom vented			
	Closed top and bottom vented	Open top and bottom vented		Replicates			Average of replicates	Replicates			Average of replicates
				1	2	3		1	2	3	
	Ounces	*Ounces*	*Inches*	*Ounces*	*Ounces*	*Ounces*	*Ounces*	*Ounces*	*Ounces*	*Ounces*	*Ounces*
Methyl bromide.......	60.80	60.80	0	13.6	16.3	17.7	15.9	2.7	4.1	5.5	4.1
			36	6.8	10.9	9.5	9.1	6.8	8.1	24.5	13.1
			72	4.1	4.1	T	2.7	2.7	2.7	9.5	5.0
Carbon tetrachloride - methyl bromide (9-1)		15.2[2]									

[1] Analysis by thermal conductivity method.

[2] Survival in surface layer: rice weevil, 93 percent; flour beetle, 100 percent.

TABLE 8.--Penetration of methyl bromide into milled products as evidenced by mortality of test insects and methyl bromide recovered at various depths

Bran

Fumigant mixture	Maximum dosage rate tested	Depth in product	Mortality of test insects				Amount of methyl bromide recovered after 20 hours	
			Sealed chamber		Open-top chamber			
			Rice weevil	Flour beetle	Rice weevil	Flour beetle	Sealed chamber	Open-top chamber
	Oz. per 1,000 cu. ft.	*Inches*	*Percent*	*Percent*	*Percent*	*Percent*	*Oz. per 1,000 cu. ft.*	*Oz. per 1,000 cu. ft.*
Ethyl acetate - methyl bromide (9-1)	171.8	0	100	100	100	100	36.4	5.2
		18	100	100	100	100	--	--
		36	100	100	100	67	10.0	6.2
		54	97	0	0	3	--	--
		72	0	0	0	3	2.6	0
n-propyl acetate - methyl bromide (9-1)	100.17	0	100	100	100	100	16.8	2.0
		18	100	100	100	100	--	--
		36	100	100	10	3	2.8	2.0
		54	0	0	0	0	--	--
		72	3	0	3	3	0.4	0
n-butyl acetate - methyl bromide (9-1)	126.88	0	100	100	100	100	21.8	2.6
		18	100	100	100	100	--	--
		36	100	100	100	0	7.2	2.2
		54	0	0	0	7	--	--
		72	0	3	10	3	0.2	0
Methyl bromide....	151.0	0	100	100	100	100	22.1	0.8
		18	100	100	100	100	--	--
		36	100	100	10	0	6.6	0.6
		54	0	3	0	0	--	--
		72	0	3	0	0	0	0
Shorts								
Ethyl acetate - methyl bromide (9-1)	171.8	0	100	100	100	100	21.0	2.0
		18	100	100	90	7	--	--
		36	100	13	10	3	2.4	0.2
		54	7	0	13	0	--	--
		72	3	3	3	0	0	0
n-propyl acetate - methyl bromide (9-1)	100.16	0	100	100	100	100	11.8	0.4
		18	100	100	97	0	--	--
		36	7	7	0	3	0.6	0
		54	0	3	3	7	--	--
		72	0	7	0	7	0	0
n-butyl acetate - methyl bromide (9-1)	125.28	0	100	100	100	100	14.4	1.4
		18	100	100	100	0	--	--
		36	10	10	10	3	0.4	0
		54	23	3	0	7	--	--
		72	13	0	0	3	0	0
Methyl bromide....	150.4	0	100	100	100	100	9.0	0.4
		18	100	100	37	3	--	--
		36	30	0	27	0	1.6	0.6
		54	17	0	10	10	--	--
		72	3	0	17	3	0.4	0.2

TABLE 8.--Penetration of methyl bromide into milled products as evidenced by mortality of test insects and methyl bromide recovered at various depths--Continued

Shorts--Continued

Fumigant mixture	Maximum dosage rate tested	Depth in product	Mortality of test insects				Amount of methyl bromide recovered after 20 hours	
			Sealed chamber		Open-top chamber			
			Rice weevil	Flour beetle	Rice weevil	Flour beetle	Sealed chamber	Open-top chamber
	Oz. per 1,000 cu. ft.	*Inches*	*Percent*	*Percent*	*Percent*	*Percent*	*Oz. per 1,000 cu. ft.*	*Oz. per 1,000 cu. ft.*
Carbon tetra - chloride - methyl bromide (9-1)	304.0	0	100	100	100	100	--	--
		18	100	100	100	100	--	--
		36	100	100	83	100	--	--
		54	67	0	43	3	--	--
		72	17	0	33	6	--	--
Middlings								
Ethyl acetate - methyl bromide (9-1)	172.96	0	100	100	100	100	16.8	2.8
		18	100	100	100	100	--	--
		36	100	100	100	100	5.8	5.2
		54	23	0	10	0	--	--
		72	20	3	20	3	0.4	0
n-propyl acetate methyl bromide (9-1)	170.56	0	100	100	100	100	22.8	1.8
		18	100	100	100	100	--	--
		36	100	100	100	0	6.6	3.2
		54	37	0	10	0	--	--
		72	40	0	10	7	0	0
n-butyl acetate - methyl bromide (9-1)	169.92	0	100	100	100	100	27.8	1.8
		18	100	100	100	100	--	--
		36	100	100	100	13	4.6	1.4
		54	33	3	43	3	--	--
		72	60	6	46	0	0	0
Methyl bromide.....	304.0	0	100	100	100	100	50.2	2.8
		18	100	100	100	100	--	--
		36	100	100	57	0	9.2	1.2
		54	26	3	23	3	--	--
		72	13	0	26	3	0	0
Flour								
Ethyl acetate - methyl bromide (9-1)	172.96	0	100	100	100	100	23.0	0
		18	100	100	20	3	--	--
		36	10	0	12	0	0	0
		54	7	0	3	0	--	--
		72	0	0	13	0	0.6	0
n-propyl acetate methyl bromide (9-1)	170.56	0	100	100	100	100	22.2	0.6
		18	100	100	100	46	--	--
		36	100	0	0	0	1.8	0
		54	13	7	0	0	--	--
		72	3	0	17	3	0	0

TABLE 8.--Penetration of methyl bromide into milled products as evidenced by mortality of test insects and methyl bromide recovered at various depths--Continued

Flour--Continued

Fumigant mixture	Maximum dosage rate tested	Depth in product	Mortality of test insects				Amount of methyl bromide recovered after 20 hours	
			Sealed chamber		Open-top chamber			
			Rice weevil	Flour beetle	Rice weevil	Flour beetle	Sealed chamber	Open-top chamber
	Oz. per 1,000 cu. ft.	*Inches*	*Percent*	*Percent*	*Percent*	*Percent*	*Oz. per 1,000 cu. ft.*	*Oz. per 1,000 cu. ft.*
n-butyl acetate - methyl bromide (9-1)	169.92	0	100	100	100	100	30.4	0.2
		18	100	40	100	33	--	--
		36	100	10	7	3	5.2	0
		54	10	17	17	7	--	--
		72	3	7	3	0	1.6	0
Methyl bromide....	304.0	0	100	100	100	100	52.8	0.8
		18	100	100	96	7	--	--
		36	100	100	0	0	5.6	0.8
		54	3	13	10	3	--	--
		72	0	3	7	0	0	0.6

TABLE 9.--Penetration of methyl bromide into milled products as evidenced by the mortality of test insects, and methyl bromide recovered at various depths, in test chambers with the top and bottom vented

Middlings

Fumigant	Maximum dosage rate tested	Depth in product	Mortality of test insects				Amount of methyl bromide recovered after 20 hours	
			Closed-top and bottom vented		Open-top and bottom vented			
			Rice weevil	Flour beetle	Rice weevil	Flour beetle	Bottom vented	Top and bottom vented
	Oz. per 1,000 cu. ft.	*Inches*	*Percent*	*Percent*	*Percent*	*Percent*	*Oz. per 1,000 cu. ft.*	*Oz. per 1,000 cu. ft.*
Methyl bromide....	304.0	0	100	100	100	100	62.4	1.2
		18	100	100	100	100	--	--
		36	100	100	70	0	10.4	0.8
		54	3	3	10	3	--	--
		72	10	0	20	0	0	0

Flour

Fumigant	Maximum dosage rate tested	Depth in product	Rice weevil	Flour beetle	Rice weevil	Flour beetle	Bottom vented	Top and bottom vented
Methyl bromide....	304.0	0	100	100	100	100	40.0	0
		18	100	100	97	10	--	--
		36	100	13	0	0	3.8	0
		54	3	0	7	7	--	--
		72	3	0	3	3	2.4	0

greater amounts of methyl bromide present at the various levels when used in mixture with ethyl acetate, or undiluted, than was present in sealed or open-top chambers as shown in table 5.

Further, when the bottom of an open-top chamber was vented, the efficiency was increased markedly, as evidenced by undiluted methyl bromide reaching the bottom level in lethal concentrations (table 7). The dosage of the carbon tetrachloride - methyl bromide mixture causing complete mortality in the bottom level was less than half that required in test chambers without a bottom vent (table 5). In fact, the downward penetration was apparently so rapid that practically no mortality resulted in the surface layer. This effect was not evident when the bottom of a sealed-top chamber was vented.

The amounts of methyl bromide recovered at the surface, middle, and bottom layers of sealed and open-top chambers also gave further insight on the behavior of this fumigant when applied to the surface. The amounts recovered in the sealed chamber at the end of the 20-hour exposure were much lower at the bottom level than at the middle and top levels (table 5). This would be the expected distribution as the bottom would be the last level to be reached by the vapors. The amounts found at the end of a 20-hour exposure in relation to the amount applied are not out of line with previous experience. Phillips found about 10 to 25 percent of the applied dosages of methyl bromide remaining in wheat after 24 hours exposure.[3]

Milled products. The results of tests with milled products are presented in tables 8 and 9.

The penetration of methyl bromide into milled products from surface applications was very slight. Even at dosage levels somewhat greater than applied to wheat, complete mortality was not attained much below the middle level.

The amounts of methyl bromide recovered at the surface, middle, and bottom level at the end of the 20-hour exposure, followed the pattern found in wheat. In the sealed test chamber the concentration at the surface was relatively high, but in the open-top test chamber the concentration was low, indicating that the fumigant vapor had escaped through the open top.

The venting of the bottom did not improve penetration as it did in the open-top test chamber filled with wheat. In fact, the loss of methyl bromide through the open top was apparently so great that the penetration was not equal to that obtained in the sealed test chamber.

In general, the smaller the particle size of the commodity the more difficult the effective penetration because of the greater surface area available for sorption. There are, of course, other variables: for example, the shorts contained much of the wheat germ which has a high fat content; materials which have a high fat content are considered to have a high methyl bromide sorptive value; methyl bromide can combine chemically with proteins.[4]

FORCED RECIRCULATION OF FUMIGANTS THROUGH BULK GRAIN

Procedure

Methyl bromide and the mixture of ethyl acetate and methyl bromide (9-1) were recirculated through the 6-foot column of wheat in the test chambers provided with recirculation ducts, to determine whether or not the presence of the diluent lessened the amount of methyl bromide sorbed by the commodity and thus increased its efficiency.

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[3] Phillips, G. L. 1955. Grain fumigation. Agr. Chem. X (1): 55-56, 117-121: X (2): 41-43, 133, 135, Jan., Feb.

[4] Brown, A. W. A. 1951. Insect control by chemicals. John Wiley and Sons, Inc. New York. 817 pp. Illus. Pages 38-39.

On the basis of the minimum dosage required in space fumigation with no commodity present (table 4), a dosage of methyl bromide of 8 ounces per 1,000 cubic feet was selected as being near the minimum lethal amount required in the presence of a commodity where sorption would take place. The dosage of the mixture was selected to give the same amount of methyl bromide, i.e., 80 ounces per 1,000 cubic feet (8 ounces of methyl bromide and 72 ounces of ethyl acetate). Gas samples at the 10-minute and 20-hour exposure periods were analyzed by the modified Volhard method and checked with the thermal conductivity gas analyzer.

The fumigants were volatilized before introduction into the return duct in one series of tests, and applied as chilled liquids to the surface of the wheat in another series.

The air flow rate through the wheat (1.616 bushels) was approximately 0.93 cubic feet per minute, or 0.575 cubic feet per minute per bushel.

Cages of test insects were inserted at the surface, and at the 18-, 36-, 54-inch, and bottom levels as in the previous tests.

A third series of tests was also conducted to determine whether a circulation cycle might be set up by natural convection stimulated by the presence of the fumigant, if a return duct system were supplied for that purpose. These tests were performed in the recirculation chambers as above except that the blowers were not operated. The formulations were applied at the same dosage as above, and in the same manner.

Results

The results of the tests in which the fumigants were recirculated are presented in tables 10 and 11. Recirculating the fumigants was more efficient than the conventional

TABLE 10.--Comparative concentrations of methyl bromide present, and mortality of test insects following recirculation of methyl bromide, and of a mixture of ethyl acetate and methyl bromide (9-1) in wheat; the same amount of methyl bromide being applied in each instance

Fumigant	Number of replications	Average concentration of methyl bromide present		Average mortality of test insects	
		10 minutes	20 hours	Rice weevil	Flour beetle
		Oz. per 1,000 cu. ft.	*Oz. per 1,000 cu. ft.*	*Percent*	*Percent*
Fumigants volatilized before introduction					
Methyl bromide.....	6	9.4	2.6	100	100
Ethyl acetate - methyl bromide (9-1)	4	9.9	2.5	100	100
Fumigants applied as chilled liquids to grain surface					
Methyl bromide.....	4	9.6	2.7	100	100
Ethyl acetate - methyl bromide (9-1)	4	8.8	2.5	100	100

TABLE 11.--Average concentration of the methyl bromide component at various levels in wheat columns following recirculation

Fumigant	Number of replications	Depth in wheat	Average concentration of methyl bromide after 20 hours
		Inches	*Oz. per 1,000 cu. ft.*
Methyl bromide...............	6	0	2.8
		18	2.3
		36	2.6
		54	2.7
		72	2.8
Ethyl acetate - methyl bromide (9-1)	4	0	2.2
		18	2.4
		36	2.6
		54	2.6
		72	2.8

method of applying them to the grain surface and depending upon natural diffusion for distribution. The complete mortality resulting from a dosage rate of the methyl bromide component of 8 ounces per 1,000 cubic feet compares very favorably with rates ranging from 48.64 to 167.20 ounces per 1,000 cubic feet in table 5 (for complete mortality of the flour beetle), and from 51.84 to 91.20 in table 6.

The sorption of methyl bromide by the wheat was approximately the same in the presence of ethyl acetate as in that of methyl bromide only, if it is assumed that the decrease from the 10-minute concentration to the 20-hour concentration is due to sorption.

Good distribution by convection occurred when a return duct was provided (table 12) and the mixture was applied to the surface of the grain, as evidenced both by the complete mortality of test insects at all levels from top to bottom, and by the rather uniform distribution of the methyl bromide component at the 20-hour period. The distribution of methyl bromide alone was more uniform than that shown in tables 5 and 6 even though complete mortality was not attained. However, when the fumigants were applied as vapors in the return duct, they apparently diffused downwards in the duct and partially penetrated upwards into the grain mass.

TABLE 12.--Distribution of the methyl bromide component in test chambers with a return duct, when applied without recirculation

Fumigant	Depth in wheat	Mortality of test insects				Concentration of methyl bromide after 20 **hours**	
		Surface application		Applied in duct			
		Rice weevil	Flour beetle	Rice weevil	Flour beetle	When applied on surface	When applied in duct
	Inches	*Percent*	*Percent*	*Percent*	*Percent*	*Oz. per 1,000 cu. ft.*	*Oz. per 1,000 cu. ft.*
Ethyl acetate - methyl bromide (9-1)	0	100	100	14	3	3.0	0.7
	18	100	100	54	0	4.2	1.1
	36	100	100	100	5	2.7	2.5
	54	100	100	100	100	3.1	5.0
	72	100	100	100	100	3.5	5.5
Methyl bromide..............	0	100	100	1	3	3.0	0.9
	18	100	100	20	6	2.7	0.9
	36	100	100	100	57	1.6	2.1
	54	74	1	100	100	2.5	3.9
	72	100	3	100	100	3.5	3.9

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